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# Chronology, Magnitude and Paleolimnological Record of Changing Metal Fluxes Related to Atmospheric Deposition of Acids and Metals in New England

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16. ABSTRACT Zinc and lead concentrations and deposition rates in sediments of three New England lakes began increasing(but at different rates) ca. 1860-1880. Maximum concentration increases range from 2 to 10 times background. Sediment concentrations of Ca and Mn decline concurrently with the increase in heavy metals. These processes are attributed to increased loading of metals and acids from precipitation since that time. Maximum deposition rates of Pb and Zn range from 1 to 3 $\mu g\text{-}cm^{-2}\text{-}y^{-1}$ for the three lakes. Maximum deposition rates for Pb occur in the youngest sediment. However, recent sediments are depleted of Zn in spite of increased atmospheric loading. Watershed contribution and in-lake focusing processes cause non-uniform deposition of metals. Allochthonous alkali-leached but heavy-metal-laden detritus has strongly influenced sediment chemistry in acidified watersheds for $\geq$ 100 years. Additionally, lakewater-sediment interactions may sensibly alter sediment chemistry (Ca, Mn, and possibly Zn) and water chemistry(Al, Mn, and Zn) as the lakes become acidified.

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# CHAPTER 2

# Chronology, Magnitude and Paleolimnological Record of Changing Metal Fluxes Related to Atmospheric Deposition of Acids and Metals in New England

J.S. Kahl
S.A. Norton
J.S. Williams

**The chemistry of nondystrophic oligotrophic lakewaters in New England is controlled primarily by bedrock lithology and atmospheric deposition. Secondarily, soil properties, hydrology and in-lake biological processes are often important. Surface water pH values covary with Na, K, Ca and Mg concentrations, which are determined by the availability of easily weathered minerals in the soil or bedrock, and by groundwater residence time in chemically resistant terranes. The resultant pH affects the solubility of Fe, Mn and Al hydroxides, and Zn and Cd adsorption/desorption reactions, and therefore determines the concentrations of these and chemically similar elements in surface waters [1].**

**No long-term studies of the chemistry of lakewaters in New England are available to evaluate long-term effects of atmospheric deposition of increasing amounts of acids and metals on lakewater chemistry. A lake sediment record, in conjunction with an understanding of sediment–water interactions, enables us to reconstruct the chronology of increasing atmospheric deposition of acids and metals, in lieu of a long-term precipitation and surface water chemical record. Reported here is an interpretation of sediment chemistry profiles from three oligotrophic, clearwater, acidic lakes with undisturbed drainage basins. In addition, initial findings of experimental studies designed to determine the influence of recent lake acidification on these sediment profiles are presented.**



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Acidification of precipitation (and subsequently groundwater, streams and lakes) with a strong acid ($H_2SO_4$ and/or $HNO_3$) should result in increased release of all cations from desorption reactions or weathering. For example, Hanson et al. [2] found that in areas receiving lower-pH precipitation in the area from New England to the Gaspé Peninsula, Quebec, the organic soils of spruce-fir forests had significantly lower concentrations of Ca, Mg, Zn and Mn. This depletion was attributed to accelerated leaching of these metals.

Superimposed on accelerated chemical weathering responses to precipitation acidification are the effects of increased atmospheric loading of metals (especially Pb and Zn). Numerous studies [3–6] of lake sediment cores infer that atmospheric deposition of Pb, Zn and other trace metals has recently increased significantly in eastern North America. Chemical analysis of dated sediment shows that the trace metal flux to sediments increased at least 100 years ago [5,7]. The atmospheric deposition of metals varies regionally; locally, metal enrichment in the sediment is a function of sedimentation rate, background metal concentration, sediment focusing and other often poorly understood factors.

Elevated levels of Pb are found in soils receiving deposition of acids and heavy metals [2,8,9]. Although archived soils are not available for comparative studies, Siccama and Smith [9] report increases in Pb over a 16-year period in forest soils in Massachusetts. Hanson et al. [2] report a gradient of Pb content in the organic matter of subalpine fir forest organic soils from southern Vermont (high Pb) to the Gaspé Peninsula (low Pb). The precipitation pH gradient ranges from about 4.1 (weighted annual mean) in southern Vermont [10] to about 4.6 in the Gaspé area [11]. Data from Semonin et al. [10] in conjunction with Lazrus et al. [12] suggest that trace metal deposition correlates with acid deposition.

Sediment deposited in the deeper part of lakes is derived in part from the terrestrial ecosystem and resuspended littoral sediments. Thus, as precipitation becomes more acidic and metal-laden, the sediments should reflect terrestrial changes—decreased concentrations of easily mobilized metals (Zn, Mn, Ca and Mg)—and increased concentration of Pb. Acidification of surface water may also cause chemical changes in this detritus before sedimentation, as well as increased in situ leaching of lake and stream sediments.

## METHODS

### Lake Selection

Little Long Pond, Dream Lake and Unnamed Pond (Figure 1) (summer pH 5.5, 4.5, and 4.5, respectively) are typical acidified lakes from a larger group of New England and Scandinavian lakes that have been studied in the past six years. However, their respective topographies and bathymetries (Table I) result in somewhat different sediment chemistry. The criteria for lake selection were:

1. Noncalcareous bedrock: the three ponds are situated in till or glacial outwash, on granite bedrock.

2. Relatively undisturbed watershed: none of the watersheds has been lumbered in the past 50–100 years, and none has any human habitations in the drainage basin.
3. No major geographic or anthropogenic dissimilarities, such as proximity to industrial plants or to saltwater (localized atmospheric input).

## Paleolimnology

Sediment cores (0.4–0.6 m) were obtained from the deepest point of each lake with a 10-cm-diameter piston corer [13] operated from a raft. All cores that were used had undisturbed sediment/water interfaces and intact stratigraphies. The cores were sectioned in the field in 0.5-cm increments from 0 to 20 cm depth in the core and in 1.0-cm increments below 20 cm depth. The samples were stored in plastic bags in the dark at 4° C until processing.

Sediment for metal analysis is dried at 110° C for 24 h, crushed, and ashed

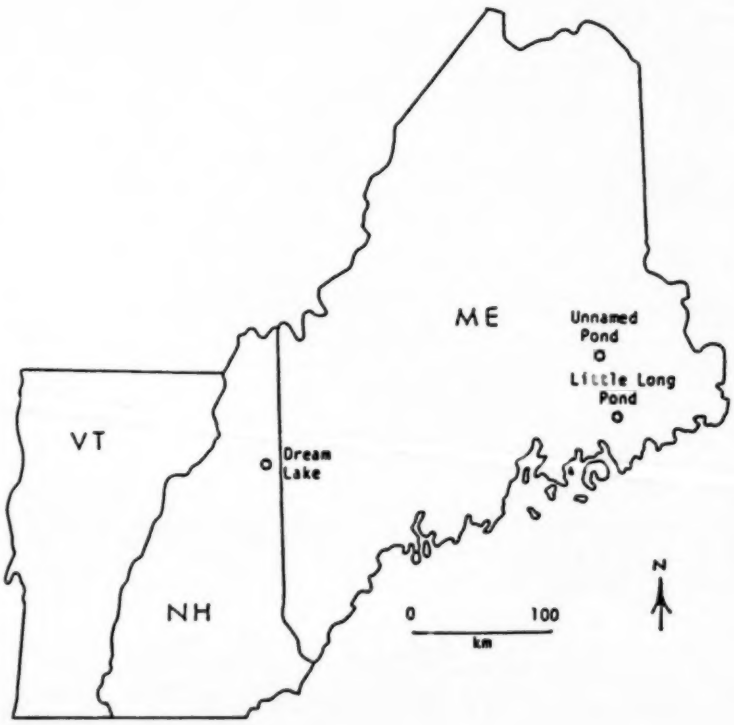


**Figure 1. Locations of study lakes.**

**Table I. Lake Characteristics**

| | *Drainage Basin Area (ha)* | *Lake Area (ha)* | *Maximum Depth (m)* | *Altitude (m)* | *Longitude* | *Latitude* |
|---|---|---|---|---|---|---|
| Dream Lake, NH | 25 | 3.7 | 1.5 | 792 | 71°06' E | 44°27' N |
| Little Long Pond, ME | 145 | 31 | 24 | 72 | 68°05' E | 44°38' N |
| Unnamed Pond, ME | 8 (Kettle) | 8 | 7 | 141 | 68°11' E | 45°12' N |

at 550° C for 3 h. A 100-mg aliquot of ashed sediment is acid-digested in a HF–aqua regia solution for 1 h at 90° C, and brought to 100 mL volume in 6% v/v HF, 1% v/v aqua regia and 5.6% w/v $H_3BO_3$ (to dissolve insoluble metal fluoride salts) [14].

Sediment chronologies were determined using the nuclide $^{210}Po$, which is a daughter product in the decay series involving $^{222}Rn$. $^{222}Rn$ is released from rocks and soils as a result of the decay of $^{226}Ra$. $^{210}Pb$ is scavenged by precipitation (maximum residence time one week) [15] and incorporated rapidly into soils [16] or onto suspended particulates in aqueous media [17]. Terrestrial lead is chemically immobile [18]; most Pb deposited in sediments has been demonstrated to have fallen directly on the lake [17]. A steady-state delivery of $^{210}Pb$ to the sediment should produce an exponential decay (concentration) curve, which decreases to nearly background in approximately 100 y (the half life for $^{210}Pb$ is 22.2 y). Sediment used for $^{210}Pb$ dating is first heated to 600° C to extract the granddaughter ($^{210}Po$) of $^{210}Pb$ [19]. $^{210}Po$ (and reference $^{208}Po$) is collected on glass wool, leached with nitric acid and put into an HCl solution by heating. The Po is then autoplated onto silver discs and counted for 20,000 s with an Ortec surface barrier detector.

## Experimental Studies

Sediment/water cores (6.35 cm diameter; 15 cm of sediment with 1 L of overlying water) were obtained with scuba for pH manipulation studies to assess metal mobilization from sediments. These cores were aerated at 4–6° C; the pH of overlying water was adjusted with mixed $H_2SO_4$ + $HNO_3$ (1:1), to achieve several pH values ranging from 3.9 to 6.5 (realistic natural pH values). All treatments, including controls, were done in triplicate and lasted for nine months. Overlying waters were sampled periodically, acidified to pH $\leq 2$ in acid-washed LPE bottles, and stored in the dark at 3–5 C until chemical analysis.

Analyses of waters and sediment digestions were performed on a Perkin-Elmer model 703 Atomic Absorption Spectrometer using standard flame or graphite

furnace (HGA-2200) techniques. The following parameters were monitored: pH, Ca, Mg, K, Na, Mn, Zn, Pb and Al.

## THE SEDIMENT RECORD

Figures 2, 3 and 4 show chemical profiles of profundal sediments of three lakes in northern New England (Figure 1, Table I). Major element concentrations and deposition rates indicate steady-state conditions in Dream and Little Long, or long-term natural changes in Unnamed, where increasing diatom abundance (flux) may have altered relative concentrations of other constituents by dilution with silica. Increases in concentrations of Pb and Zn in these sediments are concurrent with the beginning of decreasing concentrations of Ca and Mn. Based on $^{210}Pb$ chronology, the increase in heavy metals begins about 1860–1880 (Figure 5), which are reasonable dates for the onset of major industrialization and therefore atmospheric emissions in the United States. Apparent Pb atmospheric inputs to the lakes have continued to increase nearly to the present, giving rise to deposition rates as high as 3.25 $\mu g\text{-}cm^{-2}\text{-}y^{-1}$ (in Little Long, Table II). These sediments

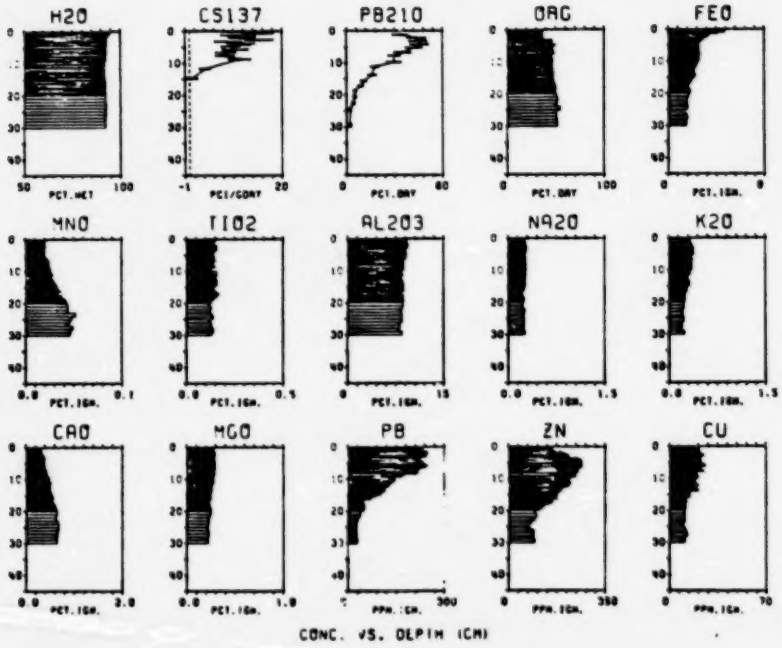


**Figure 2.** Sediment chemistry: Little Long Pond, Maine.

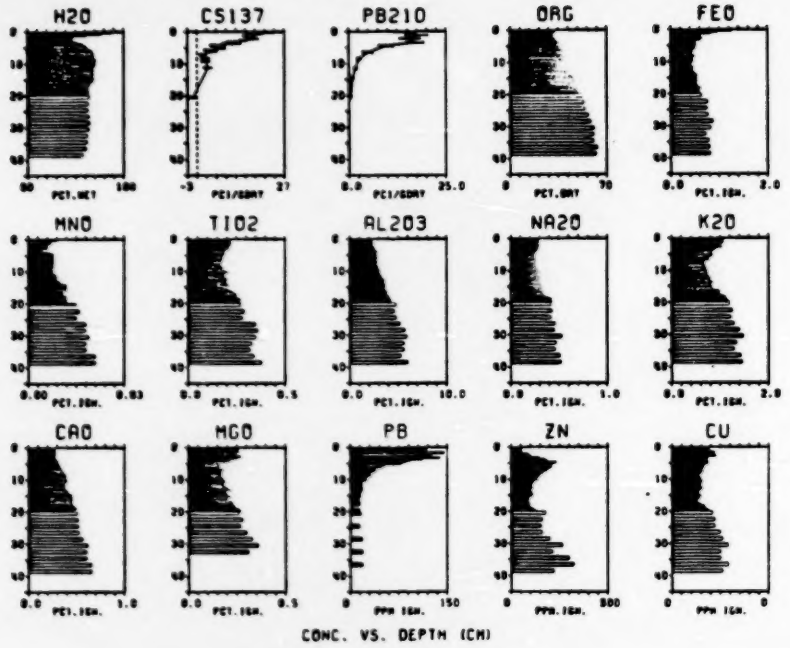


**Figure 3.** Sediment chemistry: Unnamed Pond, Maine.

have been enriched in Pb by as much as a factor of 10 over background concentrations. Zinc enrichment is as great as threefold (Table II). It is possible that hydrogen ion inputs began increasing concurrently with the heavy metals in the mid-1800s. If this is so, the Ca and Mn decrease in progressively younger sediments (Figure 5) may be due to acid leaching of soil detritus. Zinc shows decreasing sediment concentrations beginning 20–50 years ago, indicating that Zn mobilization from soils may occur at a lower pH than does Ca or Mn mobilization, or that some Zn is leached from recent sediments as the lakes become acidified. Experiments indicate that zinc is more mobile than Pb and may not be deposited in sediments after mobilization if subjected to low ambient pH in the water column.

Maximum sediment deposition rates for Pb and Zn are very similar for individual lakes (Table II), although Zn is generally more concentrated than Pb in precipitation [12]. This discrepancy suggests higher Zn loss from the watershed, which is borne out by surface water chemistry for these lakes; total dissolved Pb is normally $\leq 1$ ppb whereas total Zn is normally 5–20 ppb. The total anthropogenic Pb and Zn in Little Long sediment is markedly higher than in the other two ponds (Table II). There is no evidence for higher-than-average atmospheric inputs to the pond,

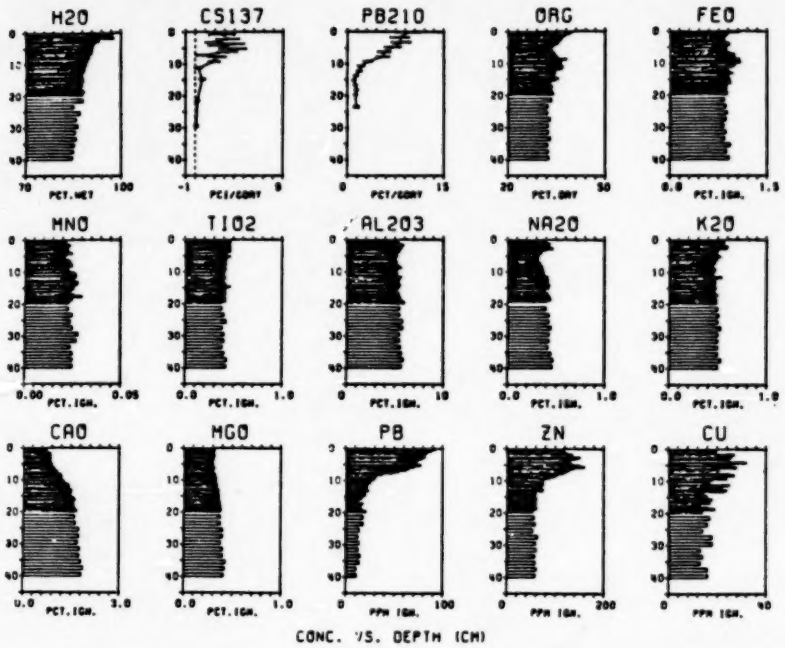


**Figure 4.** Sediment chemistry: Dream Lake, New Hampshire.

implying that focusing of sediment rich in Pb and Zn occurs in Little Long, resulting in higher Pb and Zn concentrations in deep water sediments. Consistent with this, littoral sediments are impoverished in Pb relative to profundal sediments (Figure 6). It is likely that the total anthropogenic Pb input per square meter for the entire lake bottom is nearly the same for all three ponds (as suggested by Dillon and Evans [20] for some Canadian lakes) but that it is distributed differently within each lake. Dillon and Evans [20] also report that increasing Pb concentrations are correlated with increasing depth in lakes. However, redistribution of bulk sediment does not alter concentration profiles. There must be a chemical focusing or a particulate fractionation for Pb (there may be different processes for other metals) that result in Pb-rich sediments being deposited in bathymetric lows. For example, atmospherically deposited Pb may be attached to, or rapidly scavenged by, small particulates in the water, which are preferentially deposited in deeper water. Of the elements investigated, only Pb is strongly focused.

The variability of sediment chemical profiles from different depths within the same lake (e.g., this study and Dillon and Evans [20]) suggests that great caution must be taken when generalizing from one core to an entire lake.

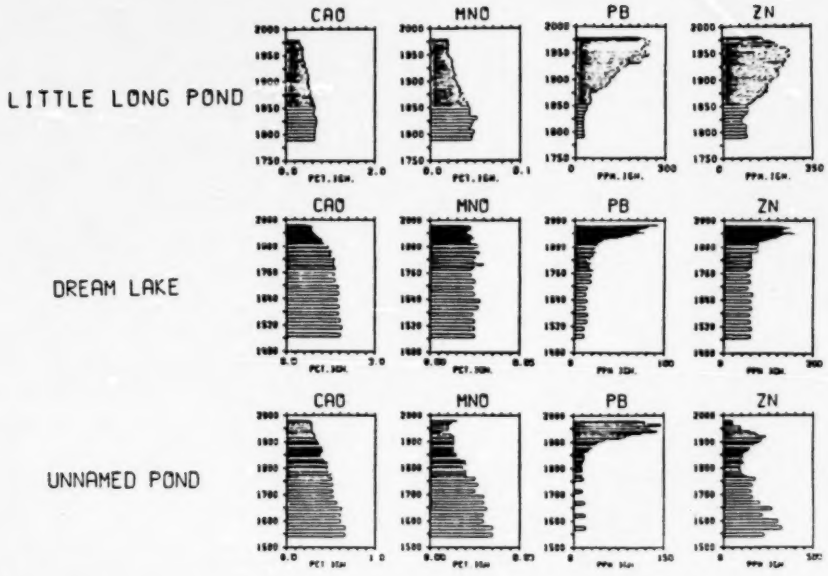


**Figure 5.** Selected sediment chemistry profiles vs time in study lakes. Dates are based on $^{210}Pb$ chronology as discussed in text.

## DISCUSSION

### Terrestrial Leaching

The decline in sediment concentration of Ca and Mn in the three lakes is generally concurrent with the increased loading of Pb and Zn, which is ubiquitous and nearly synchronous (1860–1880) across northern New England. Whether loss of these elements from the detritus occurs on the terrestrial landscape or in contact with stream or lakewater is not well understood.

In essentially all clearwater lakes in the northeastern United States, the water has a significantly higher pH than does the precipitation, due to chemical weathering reactions between soils or bedrock and groundwater. Experimental evidence in the field [21] and in the laboratory [22] suggests that acidification of precipitation increases the rate of leaching of Ca, Mg, Mn and other elements from soils. Temporal and spatial studies of percent base saturation in soils also suggest that acidification of precipitation results in a loss of exchangeable cations from soils [23], consistent with the experimental studies. If one assumes that the data for a sediment core are typical for the whole lake and its drainage basin (a risky assumption) and if the "lost" metals in the sediment core are put into solution through time, whether from terrestrial or subaqueous leaching, the estimated increase in Ca con-

**Table II. Pb and Zn Inputs[a]**

| | *Total Anthropogenic Inputs* ($\mu g\text{-}cm^{-2}$) | | *Maximum Net Deposition Rate* ($\mu g\text{-}cm^{-2}\text{-}y^{-1}$) | | *Maximum Sediment Enrichment* | |
|---|---|---|---|---|---|---|
| | *Pb* | *Zn* | *Pb* | *Zn* | *Pb* | *Zn* |
| Dream Lake | 45 | 57 | 0.99 | 1.23 | 7X | 3X |
| Little Long Pond | 197 | 195 | 3.25 | 2.74 | 10X | 3X |
| Unnamed Pond | 54 | 48 | 1.17 | 1.28 | 8X | 2X |

[a] Total anthropogenic metal is calculated from sediment concentration profiles (water content, organic content and metal concentration) as the total micrograms of metal in excess of background in a 1- × 1-cm square column of sediment. Maximum net deposition is the greatest observed quantity above background for a particular yearly "slice" of sediment. Maximum sediment enrichment is the greatest ratio obtained (for any year) of total grams of metal divided by background grams of metal.

centration in surface waters would be on the order of 0.1 ppm or less. Other elements would have smaller absolute increases but possibly significant relative increases (e.g., the missing Mn from Little Long sediment profiles would yield an increase of approximately 20 ppb). The loss of Ca and Mn from detritus, as indicated by core studies, started in some lake/drainage basins as early as the first elevated concentrations of Pb and Zn. It seems plausible that accelerated terrestrial leaching of detritus would precede lake acidification, and that subaqueous leaching would not occur until lake acidification occurs.

The profile of Zn in recent sediments is a result of two competing processes: (1) increased atmospheric loading with time and (2) greater terrestrial and aquatic leaching due to increasingly acidic precipitation. Other lakes in northern New England (not reported here) with higher pH (>6.0) typically have Zn sediment

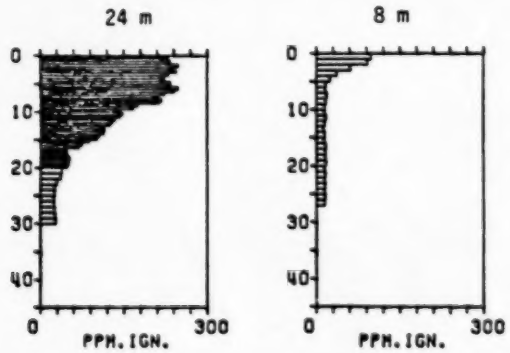


**Figure 6.** Concentration profiles of lead from 24- and 8-m depths in Little Long Pond, Maine.

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concentrations that increase to the present. Because the terrestrial detritus in New England is subjected to precipitation with weighted mean pH ≤4.4 [10], the elevated concentrations of Zn in recent sediments of higher pH lakes may be due to:

1. direct atmospheric deposition of Zn directly on the lake and subsequent sedimentation (in contrast to Zn behavior in lower pH lakes);
2. back reaction of detritus (adsorption of Zn?) with the higher pH water; or
3. a lack of leaching of sediment by lakewater.

In acidified lakes, the recent decreases may be augmented by sediment leaching or by decreased sediment scavenging.

### pH Manipulation Studies

We have manipulated the pH of the overlying water of 90 sediment/water cores taken from five lakes, including Little Long and Unnamed, to investigate possible effects of acidification on sediment and water chemistries. Our sediment chronology in conjunction with sediment chemistry presented here argues that precipitation has become progressively more "acidic" during the last 100 years, and may have been leaching soil detritus (with subsequent effects in sediments) since the mid-1800s. More recently, lakes have become acidified and the possibility of in-lake leaching has increased. Our experimental studies were to determine if in situ chemical changes may be partially responsible for the sediment profiles presented here.

Typical data from these microcosms are presented in Table III. The order of percentage increase in overlying waters is (for treatment pH 3.9) Al > Mn > Zn > Pb > Ca > Mg > K > Na. The total amount of metal released from these sediments, expressed as a percent of the total amount of the metal in the top 2 cm of the core, may be sufficient to appreciably alter sediment chemistry for some metals (Tabie IV). The order of release from sediments expressed as a

**Table III.** Changes in Concentration of Dissolved Metals in Overlying Water of pH-Controlled Sediment/Water Cores (8 m depth) from Little Long Pond, Maine

| *Initial* | *pH 3.9 9 Months* | *Percent Increase* | *pH 5.0 9 Months* | *Percent Increase* |
|---|---|---|---|---|
| Al (ppb) 50 | 2900 | 5700 | 105 | 110 |
| Zn (ppb) 20 | 195 | 875 | 34 | 70 |
| Mn (ppb) 30 | 1170 | 3800 | 10 | −67 |
| Pb (ppb) 0.5 | 3.9 | 680 | 0.5 | 0 |
| Ca (ppm) 1.5 | 9.6 | 540 | 3.1 | 106 |
| Mg (ppm) 0.4 | 1.3 | 215 | 0.7 | 73 |
| K (ppm) 0.4 | 1.1 | 165 | 0.7 | 73 |
| Na (ppm) 2.0 | 3.7 | 85 | 3.4 | 70 |

**Table IV.** Percent of Metal Reservoir Released from Top 2 cm of Sediment of Experimental Cores from Little Long Pond, Maine after 9 Months

| | *Al* | *Ca* | *K* | *Mg* | *Mn* | *Na* | *Pb* | *Zn* |
|---|---|---|---|---|---|---|---|---|
| Littoral Cores (8 m) | | | | | | | | |
| pH 3.9 | 0.8 | 22.5 | 1.4 | 5.2 | 33.7 | 1.4 | 0.4 | 14.2 |
| pH 5.0 | <0.1 | 3.2 | 0.2 | 1.4 | <0.1 | 0.2 | <0.1 | 4.0 |
| Profundal Cores (24 m) | | | | | | | | |
| pH 3.9 | 2.4 | 51.3 | 4.7 | 8.6 | 50.7 | 4.5 | 0.5 | 21.1 |
| pH 5.0 | 0.1 | 2.6 | 1.2 | 1.7 | <0.1 | 0.2 | <0.1 | 4.0 |

percentage of the sediment pool is Ca > Zn > Na ? Mg > K > Mn > Al > Pb for pH <5.0, although Mn release increases dramatically as the pH approaches 4.0. Aluminum profiles are unlikely to be perceptibly altered, due to the very large Al pool, but smaller absolute releases of Zn or Mn may be quantitatively important for trace metal profiles.

We have pointed out that concentrations of Ca, Mn and Zn decrease in younger sediments of acidic lakes. However, Ca and Mn have decreased in progressively younger sediments for at least 100 years. Assuming that lake acidification is a relatively recent event, these profiles have probably not been greatly influenced by pH-dependent diagenetic processes. Ca and Mn sediment profiles may reflect a steady decline in soil base saturation (and thus the decline in the acid-neutralizing capacity of the soil). Soils in these watersheds eventually have become sufficiently leached in conjunction with increasingly acidic precipitation to no longer function effectively as acid neutralizers, and lake acidification has ensued. We suggest that lakewaters with pH 5.0–5.5 leach Zn from sediments, and/or prevent further accumulation. Experimental work indicates that substantial release of metals from sediments at realistic pH values is possible and thus sediments may serve as a source of dissolved metals and act as acid neutralizers.

## SUMMARY

Zinc and lead concentrations and deposition rates in sediments of three New England lakes began increasing (but at different rates) ca. 1860–1880. Maximum concentration increases range from 2 to 10 times background. Sediment concentrations of Ca and Mn decline concurrently with the increase in heavy metals. These processes are attributed to increased loading of metals and acids from precipitation since that time. Maximum deposition rates of Pb and Zn range from 1 to 3 $\mu g \cdot cm^{-2} \cdot y^{-1}$ for the three lakes. Maximum deposition rates for Pb occur in the youngest sediment. However, recent sediments are depleted of Zn in spite of increased atmospheric loading. Watershed contribution and in-lake focusing processes cause nonuniform deposition of metals. Allochthonous alkali-leached but heavy-metal-laden detritus has strongly influenced sediment chemistry in acidified watersheds for

≥ 100 years. Additionally, lakewater–sediment interactions may sensibly alter sediment chemistry (Ca, Mn, and possibly Zn) and water chemistry (Al, Mn, and Zn) as the lakes become acidified.

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